

## Investigation on the Nature of Steam Modified Coal

S.D. Brandes and R.A. Graff

The Clean Fuels Institute, The City College of New York  
New York, New York 10031

### Introduction

In previous work it was found that dramatically improved liquid yields from steam pyrolysis and mild solvent extraction of bituminous coal are obtained when the coal is first exposed to subcritical steam for short periods of time (Graff and Brandes, 1984 and 1987). This finding motivated the investigation, reported here, into the nature of coal after modification by subcritical steam.

In this work solvent swelling, a technique to determine the degree of cross-linking between macromolecular units in coal (Green, et al. 1984), has been applied. An estimate of the degree of hydrogen bonding in the coal was thereby obtained.

Treated coal was also analyzed by diffuse reflectance infrared spectroscopy (DRIS) and by an o-alkylation procedure described by Liotta (1981). The results of these three studies are described in this paper.

### EXPERIMENTAL PROCEDURES

Tests were conducted using a batch of Illinois No.6 coal<sup>1</sup> ground under an inert atmosphere to pass 200 mesh and having the following elemental analysis (wt%, maf) : 76.1 C, 5.3 H, 1.3 N, 5.1 S, 11.8 O.<sup>2</sup>

#### Treatment

Treatments of coal samples were carried out in a series of fixed bed reactors. The reactors are constructed from lengths of stainless steel tubing (2.54cm X 1.35cm). The length of the tube was varied to accommodate different amounts of coal. By modifying the reactor chamber in this way these reactors can be used to treat 1.5 to 30 grams of coal at a time.

After loading, the reactor is placed horizontally so that there is a space above the coal for the flow of steam and gases evolved during treatment. The reactor is attached to a source of helium and/or steam and a thermocouple is wired to its midpoint. The reactor, including valves at either end, is wrapped in heating tape. A flow of helium at 50 atm is established through the reactor. With helium flowing at a minimal rate, controlled by an outlet needle valve, the reactor is heated to 300°C. This is above the condensation point of the superheated steam (265°C). Helium is then replaced by steam at 50 atm and the flow of steam is adjusted so

---

<sup>1</sup> We thank R. Liotta of Exxon Research and Engineering Corp. for providing this coal sample.

<sup>2</sup> Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

that there is a steady discharge of steam from the exit tube. The reactor is further heated to the desired treatment temperature in the first 2 to 3 minutes of steam flow. Treatment temperatures are in the range of 300 to 360°C. The temperature is maintained for the desired length of time (typically 15 minutes) by adjusting the voltage to the heating tape. To stop treatment, the heating tape is turned off and the steam flow replaced by helium. The reactor is allowed to cool to room temperature. The flow of helium is maintained until there is no detectable moisture in the reactor effluent. This is determined by placing a cold metal object in the flow of helium and observing any condensation which forms or by placing a piece of indicating Dryerite in the helium flow. Both inlet and outlet valves are then shut, and the tube is removed from the source of the gas.

#### Swelling

Swelling experiments were carried out as described in Green, et al. (1984). Samples of approximately 1g of coal were measured into 10mm X 80mm centrifuge tubes and covered with neoprene stoppers. The samples were centrifuged at 1700 rpm for approximately 10 minutes to settle the dry coal. The height of the sample ( $h_1$ ) was then measured by use of an external rule. Solvents were added to the tube and the tubes were capped and shaken until there was complete homogeneity. The tubes were left to stand 18 hours and then were centrifuged again until a constant height of the solid material was attained. In the case of pyridine, because of the dark color of the solution, the tube was turned upside down in order to read the height of the solids. Experiments were done under  $N_2$  in a glove bag unless the sample was to be deliberately exposed to air, then no precautions were taken in handling the sample in any step of the above procedure.

#### DRIS

Diffuse reflectance infrared spectroscopy (DRIS) was used to analyze both raw and treated coal samples which had been ground to pass 200 mesh before treating. Samples after treatment were ground and resieved, under a  $N_2$  atmosphere, to pass 200 mesh. DRIS spectra were obtained using a Nicolet 7199 instrument. Samples were handled under nitrogen in a glove bag directly attached to the sample chamber of the machine and a purge of  $N_2$  was maintained through the instrument. Data were acquired over approximately 13 minutes. The number of data points was 8192 over 1000 scans.<sup>3</sup>

#### O-Methylation

O-methylation of the treated coal was performed following procedures described by Liotta, et al. (1981). Typically, one gram of coal was weighed into a 250 ml round bottom flask immersed in an ice bath; 2.9 mmoles of tetra-n-propylammoniumhydroxide (TnPAH) were added. This was in slight excess of the 2.5 mmoles of acidic sites that were found, by titration, to be in raw coal. For treated coal the amount of TnPAH added was approximately 2.5 times this amount. Freshly distilled tetrahydrofuran (50-60 ml) was added while the contents were stirred with a teflon covered magnetic stirring bar.

---

<sup>3</sup> We thank Mr. E.W. Sheppard of Mobil Research and Development for his assistance in obtaining and interpreting the DRIS spectra.

Labeled methyl iodide ( $\text{C}^{13}\text{H}_3\text{I}$ ), in 20% excess of the amount of TnPAH that was used, was added. Stirring was continued for 72 hours. The workup entailed removing the THF on a rotovaporizer and washing the product with 250 ml of a hot methanol and water solution (1:1 by volume). The contents of the flask were then vacuum filtered on a 80 micron filter and washed with four liters of hot water. The coal was dried in a stream of nitrogen, transferred to a soxhlet extractor, and washed with distilled water for five days. The coal was then dried in a stream of nitrogen and in a vacuum oven at 90°C for 4 hours. Stable carbon isotope analyses were performed on these samples by Coastal Science Laboratories of Austin Texas using combustion techniques.

## EXPERIMENTAL RESULTS

### Swelling

Values of swelling ratios for raw and treated coals are given in Table 1. The measured increase in volume depends on the amount of material present in the solid phase. If during solvent swelling some of the solid is lost by extraction, the final volume is that of a reduced amount of material. An approximate correction for this loss can be made by dividing the swelling ratio by the fraction of starting material unextracted. This correction has been made to the values in Table 1 using average values obtained in room temperature extraction of the same samples (Graff and Brandes, 1987). By accounting for the amount of material in the solvent the swelling values of the solid phase are made comparable from one sample to the other.

In pyridine and in water the steam treated coal swells more than the raw coal or the helium treated coal by a considerable amount. In benzene the raw coal swells little more than helium or steam treated coals. Pyridine breaks hydrogen bonds, benzene does not. The difference between the degree of swelling in pyridine and in benzene is a measure of the amount of hydrogen bond cross-linking. The smaller the difference the fewer the number of hydrogen bond cross-links. In Table 2 the difference values are listed. The amount of hydrogen bond association is high for steam treated coal protected under nitrogen. The helium treated sample shows less hydrogen bonding than raw coal.

Extraction in pyridine destroys essentially all of the coal's hydrogen-bond cross-links so that subsequent swelling experiments reveal the backbone structure of the coal. It is apparent from these data that there is an increase of the degree of hydrogen bonding in the treated coal as compared to the raw and helium treated samples even in the backbone of the coal after room temperature extraction. Helium treated coal, again, shows the least amount of hydrogen bond association.

When steam treated coal is exposed to air and then swelled in pyridine the swelling ratio is decreased to below that for raw coal. Exposure of helium treated coal to air has no effect on the swelling ratio. The decrease in swelling indicates an increase of cross-links of any kind. For the air exposed samples the formation of oxygen cross-links is a possibility.

To wet steam treated coal with distilled water, 0.05% by weight xanthum gum, a polymeric thickening agent was added. When swelling experiments were conducted in water, the increase of swelling for the

treated sample over the raw coal was startling (Table 1). There is a twofold increase in the swelling value of the steam treated coal over the raw coal.

#### DRIS

Samples of coal treated in steam and helium, raw coal, and raw coal dried under vacuum at 90°C were examined by DRIS. There are no apparent differences among the samples in any region of the spectra except in the region attributed to -OH species (3200-3700cm<sup>-1</sup>) (Fig. 1). All of the spectra generated display two bands in the hydroxyl region (Fig 2). In the raw coal sample the broad peak at 3300cm<sup>-1</sup> predominates and mostly occludes the one at 3550cm<sup>-1</sup>. Vacuum drying of the coal sample at 90°C does not alter this ratio. In all the treated coal samples the peak height ratio of the two is reversed. The peak at 3550cm<sup>-1</sup> is clearly visible. The effect is evident whether the coal is treated in helium or steam, and it is not effected by exposure of the samples to air for brief times (less than ten minutes).

#### O-Methylation

The values for the relative enrichment in C-13 are given in Table 5 for raw Illinois No.6 coal, raw coal O-alkylated with labeled methyl iodide, helium treated coal, O-alkylated, and steam treated coal, O-alkylated. It is readily apparent that the steam treated coal after alkylation with the labeled methyl iodide is almost doubly enriched in C-13.

#### DISCUSSION

##### Swelling

Swelling data show that it is not a reduction of hydrogen bonding in steam treated coal that is responsible for the steam treated coal's behavior. On the contrary there is an increase in hydrogen bonding in steam treated coal. Because of the ability of water and water miscible solvents to swell the coal and the inability of water insoluble solvent to swell the coal the following conclusions have been drawn. The steam treated coal is not of the same structural makeup as the raw coal, nor as the helium treated coal. One may postulate two different structures for the modified coal. One interpretation of the data which can be made does not include any chemical interaction of the water and the coal. Residual water not removed in the drying step of the treatment process acts to hold open the coal structure. The water is miscible in pyridine and water and thus the coal swells. A possible alternative structure consists of newly formed phenolic groups created in the high pressure steam treatment. The phenols may form hydrogen bonds to each other and to the coal structure. These sites readily accept the water or water miscible solvent and cause the coal to swell more than the native structure.

#### DRIS

The apparent shift in the ratio of the two peaks which appear between 3200 and 3700cm<sup>-1</sup> in the IR spectrum provides a significant clue in determining what changes have occurred in the structure of the coal.

The broader of the two peaks, centered around 3300cm<sup>-1</sup>, is

usually associated with phenolic, alcoholic, acidic, mineral and aqueous entities in the coal structure (Fuller and Smyrl, 1985). There is no reason to believe that there is a change in the mineral matter of the coal due to steam treatment. Therefore, to interpret the observed differences between raw coal spectra and steam treated coal spectra in this region we must focus our attention on alcoholic entities, specifically phenolic -OH. The sharper peak at  $3550\text{cm}^{-1}$  in our samples may be attributed to intramolecularly bound -OH, which are higher energy, more tightly bound species. These materials have only a small amount of hydrogen bonding to other species. A comparison of these two peaks in the spectra of raw coal and treated coal shows that there is a shift in the ratio of these two peaks. It appears that the higher energy peak increases over the lower energy one. There are three ways to interpret these observations:

1. If the total number of hydroxyl groups remains fixed, then high energy species have increased at the expense of low energy species. This implies a weakening of secondary bonding, principally hydrogen bonding.

2. A decrease in the total number of hydroxyl groups would also imply a decrease in hydrogen bonding.

3. If the shift is interpreted as principally resulting from an increase in the number of high energy hydroxyl groups (the total number of hydroxyl species increasing) the amount of hydrogen bonding in the coal could have increased. The new primary hydroxyl groups (e.g. phenols), if formed at sites which in the original coal were covalently bound, would hold the structure apart and prevent reformation of the covalently cross-linked structure. This leaves a partially depolymerized coal bound only by hydrogen bonds at the new hydroxyl functionalities.

All three of these interpretations are consistent with the tenet that the coal is partially depolymerized in steam treatment. Combined, however, with the evidence from the swelling data, which indicates an increase in the degree of hydrogen bonding in the coal, the third of the above interpretations is considered most likely.

#### O-Methylation

The increased hydrogen bonding exhibited in the treated coal by the swelling experiments and the presence of a shift in the hydroxyl region of the infrared spectrum strongly indicate the presence of more OH functionality. The O-alkylation procedure, first described by Liotta (1979) has proven to be an excellent quantitative way to measure the relative abundance of these groups. The use of a traceable alkylating agent, in our case C-13 labeled methyl iodide, allows for an accurate count of the number of reacted groups. Although NH, SH, and COOH sites will also react with the alkylating agent it is safe to assume that these groups are present only in minor amounts in the coal to start with and are not altered or removed in steam treatment.

The incorporation of almost twice as many labeled C-13 groups in the steam treated coal as the raw coal and the helium treated coal substantiates the speculation that steam treated coal contains more OH groups.

## CONCLUSIONS

From these findings it is clear that steam treated coal has a structure altered from the raw starting coal. There is an inclusion of OH functionality in the structure which accounts for the increased hydrogen bonding and the shift in the IR spectrum. A tentative hypothesis for the increase in the extraction yields as well as the pyrolysis yields (both previously reported) is that these new hydroxyl sites are formed during the steam treatment at places in the original coal which were covalently bound. This leaves a partially depolymerized coal, cross-linked only by relatively weaker hydrogen bonds. These bonds are highly susceptible to water and water miscible solvents.

The quality of the resulting fuel produced from processing of this steam treated coal is expected to be substantially improved over that which would be obtainable from a raw coal. The weakened bonding structure of the coal will promote the production of lower molecular weight fragments. These, in turn, will be easier to upgrade. Preliminary findings from an investigation now underway suggest that although there is an increase in the number of hydroxyl sites it is at the expense of other organic oxygen in the coal. In other words the total organic oxygen content of the coal does not increase on steam treatment. This may indicate that the coal not only will be more easily upgraded as is mentioned above, but also, that this treated coal is not a worse feed for further processing than raw coal as it does not contain additional oxygen. A final point to be made is that the improved properties of steam treated coal are achieved with no expenditure of elemental hydrogen. This gives steam treated coal an economic headstart in upgrading to a more useful fuel.

## ACKNOWLEDGEMENTS

The use of the o-methylation technique was suggested by Martin Gorbaty of Exxon Research and Engineering Corp. We are grateful to him and to Michael Siskin, also of Exxon Research & Engineering, for helpful discussions in the course of this work.

This work was sponsored in part by the USDOE under contract No. DE-AC21-84MC21315; W.-S. Liou, Project Manager; and M. Gbate, Chief of the Gasification and Combustion Branch.

## REFERENCES

- Fuller, E.L. Jr. and N.R. Smyrl (1985), "Chemistry and Structure of Coal: Diffuse Reflectance IR Spectroscopy Equipment and Techniques", Fuel, **64**, 1143.
- Graff, R.A. and S.D. Brandes (1984), "Coal Liquefaction by Steam Pyrolysis", ACS, Division of Fuel Chemistry Preprints, **29**, (2), 104.
- Graff, R.A. and S.D. Brandes (1987), "Modification of Coal by Subcritical Steam: Pyrolysis and Extraction Yields", Energy and Fuels, **1**, 84.
- Green, T.K., J. Kovac, and J. Larsen (1984), "A Rapid and Convenient Method for Measuring the Swelling of Coals by Solvents", Fuel, **63**, 935.
- Liotta, R., K. Rose, and E. Hippo (1981), "O-Alkylation Chemistry of Coal and Its Implications for the Chemicals and Physical Structure of Coal", J. Org. Chem, **46**, 277.
- Liotta, R. (1979), "Selective Alkylation of Acidic Hydroxyl Groups in Coal", Fuel, **58**, 725.

Table 1

Swelling Ratios (Q) for Raw and Treated\*  
Illinois No. 6 Coal

<u>Solvent</u>	<u>Raw</u>		<u>Steam Treated</u>		<u>Helium Treated</u>		
	<u>In Air</u>	<u>Extracted</u>	<u>Under N<sub>2</sub></u>	<u>In Air</u>	<u>Under N<sub>2</sub></u>	<u>In Air</u>	<u>Extracted</u>
Pyridine <sup>+</sup>	2.80	1.95	3.01	2.46	1.88	2.24	1.68
Benzene	1.13	1.35	1.06	1.00	1.12	1.00	1.24
Water	0.98	1.21	1.83	1.84	0.98	1.56	1.23

\*Treatments in steam and helium for 15 minutes at 50 atmospheres

+Corrected for extraction losses

Table 2  
Difference in Swelling Ratio (Q)  
of Pyridine and Benzene Swollen Samples

	$Q_{\text{pyr}} - Q_{\text{benz}}$
Raw	
In Air	1.67
Extracted	0.60
Steam Treated	
Under N <sub>2</sub>	1.95
In Air	1.46
Extracted	0.76
Helium Treated	
Under N <sub>2</sub>	1.24
In Air	1.18
Extracted	0.44

Table 3  
Relative Ratio of C-13/C-12  
In O-Alkylated Coals

<u>Sample</u>	<u>Ratio</u>
Raw Illinois No.6	-25*
O-methylated Raw Coal	4900
O-methylated Steam Treated Coal	8240*
O-methylated Helium Treated Coal	3789

\*Average of two values



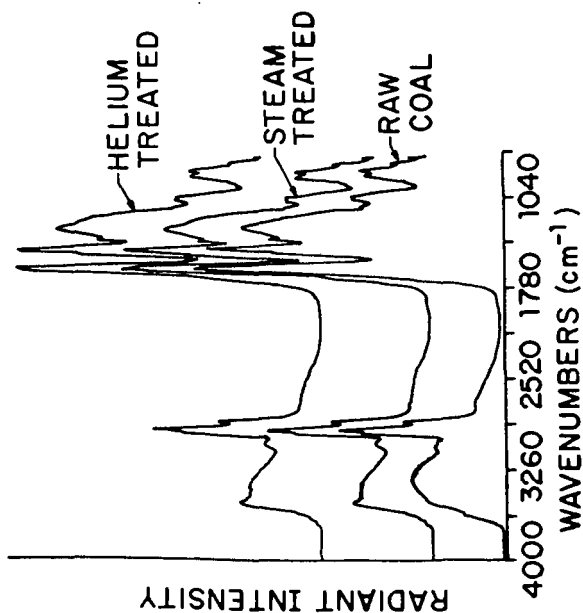


Figure 1. Comparison of DRIS Spectra of Treated Illinois No. 6 Coal

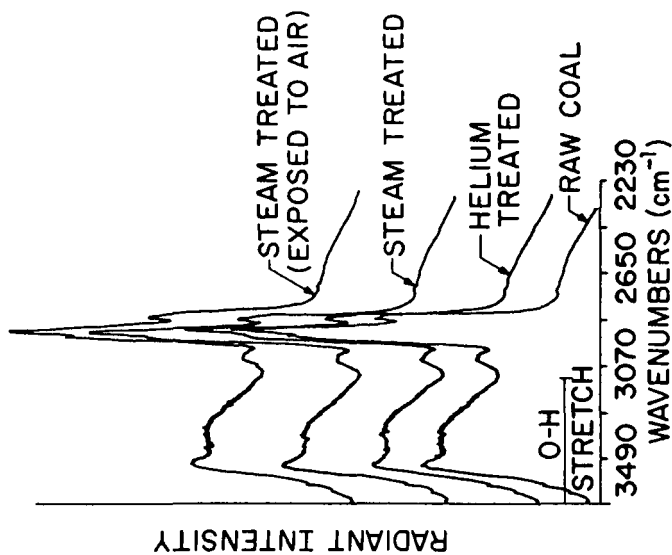


Figure 2. Comparison of the OH Stretching Region of Various Treated Illinois No. 6 Coal